1,028,923

PATENT SPECIFICATION

NO DRAWINGS

1,028,923

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Date of filing Complete Specification: March 11, 1963.

Application Date: March 22, 1962. No. 11031/62.

Complete Specification Published: May 11, 1966.

Index at acceptance:—C2 C(1E3K4, 1E3K6, 1E4K4, 1E4K6, 1F2A2, 1F2C2, 1F2C4, 1F2C5, 1F2D3, 1K2A3, 1K2B, 1K2C3, 2B3A4, 2B3B, 2B3D, 2B3G4, 2B3G8, 2B6A4, 2B6B, 2B6D, 2B6G10, 2B6J, 2B48D1, 2B48G3, 2D11, 3A7V1A4, 3A7V1E2, 3A7V1J1, 3A13C3C, 3A13C4C, 3A13C6C, 3A13C7, 3A13C9, 3A13C10D, 3C5A4, 3C5C3, 3C5C4, 3C5C6, 3C5E1, 3C5E2); C3 R(3C14, 22C14, 33C14); C5 D(6B7, 6B12E); D1 P(1C1A, 1C1B, 1C2A, 1C2B, 1C3A, 1C3D, 1C4, 1D)

Int. Cl.:—C 07 d // C 08 g, C 11 d, D 06 l

COMPLETE SPECIFICATION

Naphthalene-Substituted Heterocyclic Compounds

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new naphthalene compounds, more particularly naphthalene compounds carrying certain substituted heterocyclic substituents, and the use of these compounds as fluorescent brightening agents.

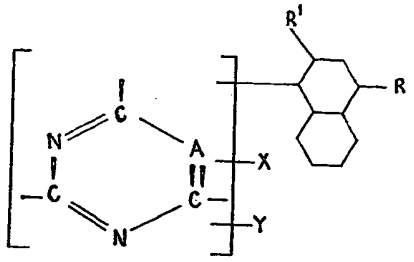
We have now found that cyanuric chloride will react with alkoxy naphthalenes in presence of a catalyst of the Friedel-Crafts type to afford 2:4 - dichloro - 6 - (alkoxy naphthyl) - 1:3:5 - triazines. The chlorine atoms in this compound may be substituted, separately if desired, by for example groups such as substituted amino or alkoxy by treatment with amines or alcohols in presence of an acid-binding agent. These dichloro compounds and the derivatives obtained by replacement of one or both chlorines have been found to be surprisingly effective as whitening agents particulary for textile materials.

Similarly 2:4:6 - trichloropyrimidine reacts with alkoxy naphthalenes to afford substituted naphthyldichloropyrimidines, usually as a mixture of the 2:4 - dichloro - 6 - (substituted naphthyl)- and 2:6 - dichloro - 4 - (substituted naphthyl)pyrimidines. These compounds can, like the corresponding triazines, be interacted with for example amines or alcohols in presence of acid-binding agents, and are effective whitening agents.

2:4:5:6 - tetrachloropyrimidine reacts similarly.

The naphthalene compounds may also be made by reacting cyanuric chloride or 2:4:6 - trichloropyrimidine with hydroxynaphthalenes in presence of a catalyst of the Friedel Crafts type to afford 2:4 - dichloro - 6 - hydroxynaphthyl - 1:3:5 - triazines or dichlorohydroxynaphthyl - pyrimidines as described in our copending Application No. 8033/62 (Serial 1028922). These compounds, or the products obtained from them by replacing the chlorine atoms with substituted amino or alkoxy groups by treatment with amines or alcohols, may be converted to 2:4 - substituted - 6 - alkoxynaphthyl - 1:3:5: - triazines or the corresponding pyrimidines by reacting with alkylating agents such as dimethyl sulphate. Similarly use of acylating agents such as acetic anhydride instead of alkylating agents affords 2:4 - substituted - 6 - acyloxynaphthyl - 1:3:5 - triazines or the corresponding pyrimidines.

According to our invention therefore there are provided new naphthalene compounds of the formula:



wherein R and R^1 each stand for a hydrogen atom or an alkoxy, aralkoxy, aryloxy, or acyl-

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oxy group not more than one of them standing for a hydrogen atom, A stands for a nitrogen atom or a group CB wherein B stands for a hydrogen atom or a chlorine atom and X and Y stand for a halogen atom or an amino, substituted amino, alkoxy, substituted alkoxy, aryloxy, mercapto or substituted mercapto group.

As groups which may be represented by R and R^1 there may be mentioned methoxy, ethoxy, higher alkoxy, acetoxy, chloracetoxy, higher acyloxy, benzyloxy and phenoxy.

As groups which may be represented by X and Y there may be mentioned chloro, bromo, amino, alkylamino, arylamino, dialkylamino, β - hydroxyethylamino, bis(β - hydroxyethyl)-amino, alkoxy, substituted alkoxy such as β - hydroxyethoxy, aryloxy or substituted aryloxy such as 4 - methoxyphenoxy, alkyl mercapto and arylmercapto.

The naphthalene compounds of our invention wherein X and Y each stand for halogen atoms may be prepared for example by interacting a cyanuric halide or 2:4:6 - trihalogenopyrimidine in approximately equimolecular proportion with a naphthalene carrying alkoxy, aralkoxy or aryloxy substituents in one or both of the 1 and 3 positions in the presence of a Friedel - Crafts catalyst such as aluminium chloride. The reaction is preferably carried out in solution, for example in benzene, carbon disulphide, tetrachlorethane, monochlorobenzene, dichlorobenzene, nitrobenzene, or dioxane at a temperature between 0 and 40°C. best yields being obtained at temperatures between 10 and 20°C.

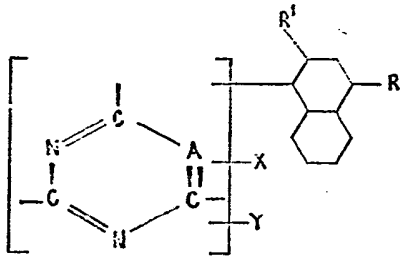
If naphthalene compounds are desired in which one halogen atom has been replaced by another group, for example a substituted amino group, the dihalogeno compound for example dichloro compound, is then interacted with approximately one molecular equivalent of an amine in presence of an acid-binding agent, which may be the amine itself, in a solvent such as acetone, toluene or water at a temperature between 20°C. and 100°C. and preferably between 50 and 100°C. If replacement of the chlorine by an alkoxy group is required, the dichloro compound is heated with the sodium derivative of the appropriate alcohol, preferably using excess of the alcohol as solvent, at a temperature conveniently between 50° and 100°C. Aryloxy or arylthio groups may be similarly introduced.

The remaining chlorine atom may be replaced by repeating the reaction with, for example, the amine or the appropriate sodium alkoxide. If both chlorines are to be replaced by the same group these two stages may of course be combined into one.

Purer dialkoxytriazinyl or pyrimidyl compounds are sometimes obtained by heating the dichloro compound with sodium phenate so as to obtain the diphenoxy compound and then heating the latter with excess of the alcohol and a catalytic amount of he corresponding sodium alkoxide.

Water soluble compounds can be obtained for example by condensing the mono or dichloro compounds with an arylaminesulphonic acid such as sulphanilic acid or alternatively by condensing with for example monoethanolamine, and sulphating the hydroxyl group of the product. Instead of sulphating the latter condensation product, its properties can be modified, for example by acetylation of the hydroxyl groups.

According to a further feature of our invention there is provided a process for the whitening of polymeric materials by the incorporation into the said polymeric material of a naphthalene compound of the formula:



wherein R, R^1, A, X and Y have the significances given earlier.

Polymeric materials which may be whitened by the process of the invention include synthetic polymeric materials, for example polyamides such as polyhexamethylene adipamide, polyesters such as polyethylene terephthalate, polyurethanes, polyacrylonitrile and hydrolysed polyacrylonitriles, polymethyl methacrylate, polystyrene, polyethylene, polypropylene, artificial polymers for example secondary cellulose acetate, cellulose triacetate and regenerated cellulose such as viscose, and natural polymers for example cellulose such as cotton and paper, silk and wool.

The preferred method of incorporating the naphthalene compounds of the invention into the polymeric material particularly when the polymeric material is a synthetic or artificial polymer, is by treating the polymeric material with an aqueous dispersion of the naphthalene compound. The aqueous dispersion is preferably substantially neutral, or slightly alkaline, but acid conditions may be employed if desired although not usually so effective. The use of substantially neutral aqueous suspensions in the process of the invention permits these whitening agents to be applied to textile materials at the same time as dispersed dyestuffs thus providing dyeings or brighter shade.

The temperature of application should be at least 40°C. In the case of secondary cellulose acetate the temperature is desirably about 85°C

since use of higher temperatures may soften the material, but with polyamides, cellulose triacetate, acrylonitrile polymers and copolymers and polyesters it is convenient to treat the polymeric material at the boiling point, 95°C to 100°C, of the aqueous suspension. Subject to any limitation imposed by the heat stability of the polymeric material higher temperatures, for example up to 140°C. under superatmospheric pressure if necessary, may be used.

Another method of application, of particular value with synthetic polymeric materials such as polyethylene terephthalate, is to impregnate the fabric with an aqueous suspension of the naphthalene compound by padding preferably at room temperature and then drying the fabric by heating in air at a temperature between 150°C. and 200°C. and preferably about 180°C. for a short period, preferably between 20 and 30 seconds.

Surface-active agents, for example fatty alcohol-ethylene oxide condensates or sulphonated alkylnaphthalenes may be added with advantage, and it is many cases convenient to disperse the naphthalene compound in a soap or detergent, which is then used to wash and whiten simultaneously the textile material from an aqueous medium. The incorporation of these compounds in soaps or detergents also improves the appearance of the soaps or detergents and this constitutes a further feature of the invention.

The naphthalene compounds may be used in conjunction with other whitening agents, for example substituted 4:4′ - ditriazinyl - aminostilbene - 2:2′ - disulphonic acids, in order to increase the whitening effect on certain textile materials, for example cotton and wool when mixtures of textile materials are being treated.

Other methods of incorporating the naphthalene compounds in the process of the invention may be used if desired. The naphthalene compounds may for example be mixed with the polymer in molten or plasticised form. Alternatively if the naphthalene compound is in the form of a water-soluble derivative, for example a sulphonic acid salt, it may be applied from aqueous solution in the conventional manner.

Particularly effective as whitening agents are those naphthalene compounds in which one of R and R^1 stands for a hydrogen atom and the other for an alkoxy group, particularly wherein R stands for a methoxy group, and in which A stands for a nitrogen atom, and X and Y each stands for a halogen atom, particularly a chlorine atom.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight unless otherwise specified.

Example 1

13.5 parts of aluminium chloride are added at a temperature between 5 and 10°C. to a stirred mixture of 15.8 parts of 1 - methoxy - naphthalene and 18.5 parts of cyanuric chloride in 120 parts of benzene. The mixture is stirred for 20 hours, the temperature being allowed to rise to room temperature and the solid is removed by filtration, washed with benzene and dried *in vacuo*. It is freed from aluminium compounds by stirring with 450 parts of ice cold water containing 5 parts of 37% aqueous hydrochloric acid, followed by filtration and washing with ice cold water. The paste is resuspended in 300 parts of water containing 2.5 parts of sodium dihydrogen phosphate and 2.5 parts of disodium hydrogen phosphate, refiltered, washed with 100 parts of water containing 5 parts each of disodium hydrogen phosphate and sodium dihydrogen phosphate and dried *in vacuo* at 50°C. to give 30 parts of a product containing 80% of 2:4 - dichloro - 6 _ (4 - methoxynaphthyl) - 1:3:5 - triazine.

2.5 parts of the above product are milled with 98 parts of water in presence of 2.5 parts of disodium hydrogen phosphate, 2.5 parts of sodium dihydrogen phosphate and 0.1 part of disodium dinaphthylmethane - disulphonate for 48 hours. Pieces, each of 1 part, of cotton, wool, polyethylene terephthalate, polyhexamethylene adipamide, cellulose triacetate and polyacrylonitrile fabrics are placed in 200 parts of water and 1.0 part of the dispersion prepared as described above is added. The water is heated at 100°C. for 1 hour. An exceptional whiteness is imparted to the polyethylene terephthalate and, to a slightly less degree, to the polyhexamethylene adipamide, cellulose triacetate and polyacrylonitrile fabrics. A similar procedure with secondary cellulose acetate carried out at 85°C. afforded similar high whiteness effects. The white effects may be built up to very high levels and have good fastness to light.

Example 2

13.5 parts of aluminium chloride are added at a temperature between 5 and 10°C. to a stirred mixture of 17.2 parts of 2 _ ethoxy-naphthalene and 18.5 parts of cyanuric chloride in 120 parts of benzene. The mixture is stirred for 20 hours, the temperature being allowed to rise to room temperature, and the solid is removed by filtration, washed with benzene and dried *in vacuo*. It is freed from aluminium compounds by stirring with 450 parts of ice cold water containing 5 parts of 37% aqueous hydrochloric acid, followed by filtration and washing with ice cold water. The paste is resuspended in 300 parts of water containing 2.5 parts of sodium dihydrogen phosphate and 2.5 parts of disodium hydrogen phosphate, refiltered and washed with 100 parts water containing 5 parts of sodium diyhdrogen phosphate and 5 parts of disodium hydrogen phosphate and finally dried *in vacuo* at 50°C. to give 27 parts of 2:4 - dichloro - 6 _ (2 -

ethoxynaphthyl) - 1:3:5 - triazine at 80% strength.

This product is dispersed in water containing phosphate buffers and a dispersing agent and used for the treatment of fabrics of polymeric materials as described in Example 1. White effects, slightly inferior to those obtained in Example 1, are produced.

EXAMPLE 3

6.4 parts of 2:4 - dichloro _ 6 - (2 - ethoxynaphthyl) - 1:3:5 - triazine are dissolved in 80 parts of acetone and a solution of 4.2 parts of diethanolamine in 24 parts of acetone is added. The mixture is stirred and raised to the boiling point for 3 hours, cooled and poured into 550 parts of iced water. The white precipitate is filtered off, washed with water and dried at 40°C. *in vacuo* to give 8 parts of 2 _ chloro - 4 - di(β - hydroxyethyl) - amino - 6 - (2 - ethoxy naphthyl) _ 1:3:5 - triazine useful as a whitening agent.

EXAMPLE 4

7.65 parts of 2:4 - dichloro - 6 - (4 - methoxynaphthyl) _ 1:3:5 - triazine are dissolved in 80 parts of acetone, and a solution of 5.3 parts of diethanolamine in 24 parts acetone is added. The mixture is stirred and raised to the boiling point for 3 hours, filtered, and the filtrate added to 500 parts of iced water. The precipitate is filtered off, washed with water and dried *in vacuo* at 40°C to give 9 parts of 2 - chloro - 4 _ di(β - hydroxyethyl) - amino - 6 - (4 - methoxynaphthyl) _ 1:3:5 - triazine. This product is found to contain 13.5% of nitrogen and 9.0% of chlorine; the theoretical values for $C_{16}H_{19}O_3N_4Cl$ are 15.0% of nitrogen and 9.5% of chlorine.

This product is dispersed in water containing a dispersing agent as described in Example 1 but without phosphate buffers and is applied to fabrics of polymeric materials as described in Example 1. White effects, very slightly inferior to those afforded in Example 1, are obtained.

EXAMPLE 5

30.6 parts of 2:4 - dichloro - 6 _ (4 - methoxynaphthyl) - 1:3:5 - triazine are stirred with 320 parts of acetone and a solution of 20 parts of phenol in 60 parts of acetone is added. The mixture is stirred and raised to boiling point and a solution of 8 parts of sodium hydroxide in 20 parts of water is added evenly over 1 hour. The mixture is stirred at the boil for a further three hours and filtered at the boil. The filtrate is cooled and the precipitated solid is collected by filtration, washed with acetone and dried at 40°C. to give 33 parts of 2:4 - diphenoxy - 6 - (4 - methoxynaphthyl) - 1.3.5 - triazine, which is a white crystalline solid melting at 154°C. This product is found to contain 10.1% of nitrogen compared with a theoretical value of 9.9% of nitrogen, and is useful as a whitening agent.

EXAMPLE 6

8.4 parts of 2:4 - dichloro - 6 _ (4 - methoxynaphthyl) - 1:3:5 _ triazine are stirred with 80 parts of acetone and a solution of 10 parts of aniline in 40 parts of acetone is added evenly over ½ hour at 20°C. The mixture is then stirred and heated to the boiling point for 18 hours, cooled and filtered. The filtrate is added to 500 parts iced water and the precipitated fawn crystals are filtered and water washed and dried at 40°C. to give 6.6 parts 2:4 - di(phenylamino) - 6 - (4 _ methoxynaphthyl) - 1:3:5 _ triazine. Recrystallisation from a mixture of 50 parts benzene and 50 parts petrol yields 2.2 parts white crystals melting at 192°C. This product is found to contain 16.6% of nitrogen compared with a theoretical value of 16.7% of nitrogen, and is useful as a whitening agent.

EXAMPLE 7

2.3 parts of sodium are dissolved in 240 parts of methanol and the solution stirred at a temperature between 0 and 5°C. and 15.3 parts of 2:4 - dichloro - 6 - (4 - methoxynaphthyl) - 1:3:5 - triazine are added portionwise over 1 hour. The mixture is then stirred and raised to the boiling point in 2 hours and maintained at that temperature for a further 16 hours. The mixture is filtered at the boil and the filtrate cooled and the white crystalline precipitate filtered, washed with acetone and dried at 40°C. to give 8 parts of 2:4 - dimethoxy - 6 _ (4 - methoxynaphthyl) - 1:3:5 - triazine melting at 118°C. This product is found to contain 13.4% of nitrogen compared with a theoretical value of 14% of nitrogen.

EXAMPLE 8

14.6 parts of aluminium chloride are added at a temperature of 20°C. to a stirred mixture of 15.8 parts of 1 - methoxynaphthalene and 18.5 parts of cyanuric chloride in 220 parts monochlorobenzene. The mixture is stirred for 20 hours and then 100 parts of water are added. The solvent is removed by steam distillation and the residual 2.4 _ dichloro - 6 - (4 _ methoxynaphthyl) - 1.3.5. - triazine is isolated by filtration and washing. The yield is 28 parts of a yellow solid similar to that obtained by the process of Example 1, which can be purified by crystallisation from acetone to give yellow crystals m.p. 143°C. Analysis gives Cl = 23.2%, N = 13.7% agreeing with the calculated values for $C_{21}H_{19}OCl_2N_3$.

EXAMPLE 9

120 parts of benzene are saturated with ammonia gas and stirred with 5 parts of 2:4 - dichloro - 6 - (4 -methoxynaphthyl) _ 1:3:5 - triazine. The steam of ammonia is continued for approximately 2 hours and the product is isolated by filtration, washing with benzene and then water and drying. 3.9 parts of crude 2 - amino _ 4 - chloro - 6 - (4 _ methoxynaphthyl) - 1:3:5 - triazine, melting between temperatures of 217 and 219°C are obtained, which on crystallisation from xylene give 2.8 parts of product melting at a temperature be-

tween 222 and 223°C. Analysis gives N 19.5% and Cl 12.5%., $C_{14}H_{11}ON_4Cl$ requires N 19.5% and Cl 12.4%.

The product may be used to whiten polyhexamethylene adipamide, cellulose acetate, polyethylene terephthalate and polyacrylonitrile.

EXAMPLE 10

0.63 parts of sodium are dissolved in 80 parts of methanol, 7.2 parts of 2 - amino - 4 - chloro - 6 - (4 - methoxynaphthyl) - 1:3:5 - triazine are added, and the mixture is heated at the boiling point for 16 hours. After cooling, the product is removed by filtration, washed with water and dried. It can be purified by crystallisation from butanol to give 4.7 parts of 2 - amino - 4 - methoxy - 6 - (4 - methoxynaphthyl) - 1:3:5 - triazine, melting between 181 and 182°C., and having the analysis:— C 63.6%, H 4.9%, N 19.9%, —OCH_3 22.6%; $C_{15}H_{14}O_2N_4$ requires:— C 63.8%, H 4.95%, N 19.8%, —OCH_3 22.0%.

The product may be used to whiten polyhexamethylene adipamide, cellulose acetate, polyethylene terephthalate and poly-acrylonitrile.

EXAMPLE 11

5 parts of 2 - amino - 4 - methoxy - 6 - (4 - methoxynaphthyl) - 1:3:5 _ triazine and 25 parts of acetic anhydride are heated together at the boiling point for 16 hours. After cooling, the product is collected, and washed with acetic acid and then methanol to give 4.2 parts of 2 - acetylamino - 4 - methoxy - 6 - (4 - methoxynaphthyl) - 1:3:5 _ triazine. It can be purified by crystallisation from toluene and then melts between 184—185°C., and has the analysis:— C 62.7%, H 4.6%, N 17.1%; $C_{17}H_{16}O_3N_4$ requires C 63.0%, H 4.95%, N 17.3%.

The product may be used to whiten polyhexamethylene adipamide, cellulose acetate, polyethylene terephthalate and poly-acryonitrile.

EXAMPLE 12

4.6 parts of sodium are dissolved in 160 parts of ethanol and the solution is saturated at 0°C. with hydrogen sulphide. 16 parts of 2:4 - dichloro _ 6 - (4 _ methoxynaphthyl) - 1:3:5 - triazine are added and the mixture is allowed to warm slowly to room temperature. It is then raised to the boiling point for 24 hours, diluted with 200 parts of water and acidified with hydrochloric acid. The yellow product is collected to give 15.7 parts of crude 2:4 - dimercapto - 6 - (4 _ methoxynaphthyl) _ 1:3:5 - triazine which is purified by crystallisation from butanol. The purified product melts between 231 and 236°C. and has the analysis:— C 55.4%, H 3.6%, N 13.9%, S 18.8%; $C_{14}H_{11}ON_3S_2$ requires C 55.8%, H 3.65%, N 14.0%, S 21.2%.

4 parts of 2:4 - dimercapto - 6 - (4 - methoxynaphthyl) - 1:3:5 - triazine are stirred in a solution of 4.8 parts of sodium hydroxide in 120 parts of water, and 11.3 parts of dimethyl sulphate are added. After several hours the mixture is filtered, and the solid washed and crystallised from ethanol to give 2.8 parts of the 2:4 - dimethylmercapto _ 6 - (4 - methoxynaphthyl) - 1:3:5 - triazine as pale cream needles melting between 114 and 116°C. Analysis gives:— C 58.3%, H 4.6%, N 12.8%, S 18.3%; $C_{16}H_{15}ON_3S_2$ requires C 59.8%, H 4.4%, N 12.3%, S 18.8%.

The product may be used to whiten polyhexylmethylene adipamide and polyethylene terephthalate.

EXAMPLE 13

9.3 parts of 1 - isopropoxynaphthalene and 9.3 parts of cyanuric chloride are stirred together in 80 parts of benzene, and 6.7 parts of aluminium chloride are added at a temperature between 0 and 5°C. After agitation for 16 hours the tarry reaction mixture is decomposed with iced water, filtered from some red insoluble matter, and the benzene layer separated washed and dried. The benzene is removed by vacuum distillation and the residue recrystallised from methyl ethyl ketone to give 4.5 parts of 2:4 _ dichloro - 6 - (4 - isopropoxynaphthyl) - 1:3:5 - triazine as pale yellow crystals melting between 126 and 128°C. Analysis gives: C57.7%, H 3.9%, N 12.8%, Cl 20.9%; $C_{16}H_{13}ON_3Cl_2$ requires: C 57.4%, H 3.9%, N 12.6%, Cl 21.3%.

The product may be used to whiten polyethylene terephthalate.

EXAMPLE 14

1.3 parts of sodium are dissolved in 120 parts methanol, 8.4 parts of 2:4 - dichloro - 6 - (4 - isopropoxynaphthyl) - 1:3:5 _ triazine are added, and the mixture is raised to the boiling point for 18 hours. The mixture is filtered and the filtrate on cooling deposits 3.9 parts of 2:4 - dimethoxy - 6 _ (4 - isopropoxynaphthyl) _ 1:3:5 - triazine as white needles melting between 88 and 89°C. Analysis gives: N 12.8%; $C_{18}H_{19}O_3N_3$ requires N 12.95%.

The product may be used to whiten polyhexamethylene adipamide.

EXAMPLE 15

11 parts of 1 - phenoxynaphthalene and 9.3 parts of cyanuric chloride are stirred together in 80 parts of benzene and 6.7 parts of aluminium chloride are added at a temperature between 0° and 5°C. The mixture is stirred for 16 hours, the complex decomposed with iced water, some insoluble matter is removed by filtration and the benzene evaporated under reduced pressure. The residue is crystallised from methyl ethyl ketone to give 8.25 parts of 2:4 - dichloro - 6 _ (4 - phenoxy - naphthyl) - 1:3:5 - triazine as pale yellow crystals melting between 152 and 153°C. Analysis: Cl 20.9%, N 11.7%. $C_{19}H_{11}ON_3Cl_2$ requires Cl 19.3%, N 11.4%.

The product may be used to whiten polyethylene terephthalate.

EXAMPLE 16

14 Parts of sodium are dissolved in 500 parts of methanol, and 76 parts of 2:4 - dichloro _ 6 - (4 - hydroxynaphthyl) - 1:3:5 - triazine are added. The mixture is heated to reflux for 48 hours, then diluted with 1200 parts of water, and 9 parts of sodium hydroxide are added and the mixture is then filtered. The filtrate is acidified with hydrochloric acid and the yellow precipitate collected and dried. 62 Parts of crude 2:4 - dimethoxy - 6 - (4 - hydroxynaphthyl) - 1:3:5 - triazine are obtained and purified by crystallisation from methanol. The purified material melts between 203 and 204°C. and contains C 63.4%, H 4.6%, N 13.5%, OCH_3 22.3%, $C_{15}H_{13}N_3O_3$ requires C 63.7%, H 4.6%, N 14.8%, OCH_3 22.0%.

5 Parts of purified 2:4 - dimethoxy - 6 - (4 - hydroxynaphthyl) - 1:3:5 _ triazine and 25 parts acetic anhydride are heated together at the boiling point for 3 hours. On cooling 2:4 - dimethoxy - 6 - (4' - acetoxynaphthyl) - 1:3:5 - triazine crystallises. It is isolated by filtration and washing with acetic acid and then petroleum ether, giving 4.9 parts of product melting between 185 and 187°C. The product is useful as a whitening agent.

EXAMPLE 17

11.6 Parts of dichloro _ (4 - hydroxynaphth - 1 - yl))pyrimidine are dissolved in a solution of 3.2 parts sodium hydroxide in 280 parts of water. The solution is stirred vigorously and 15 parts of dimethyl sulphate are added, alkalinity being maintained by periodic additions of sodium hydroxide as necessary. After 3 hours the alkaline solution is extracted with chloroform and the solvent evaporated to give a slightly oily residue. This is washed with ether and dried to give 6.1 parts of dichloro - (4 - methoxynaphth - 1 _ yl) - pyrimidine melting between 174 and 177°C. Analysis gives C 58.5%, H 2.9%, N 9.3%, Cl 22.2%, OCH_3 10.3%, $C_{15}H_{10}ON_2Cl_2$ requires C 59.1%, H 3.3%, N 9.2%, Cl 23.3%, OCH_3 10.2%.

The product may be used to whiten polyhexamethylene adipamide, cellulose acetate, polyethylene terephthalate and polyacrylonitrile.

EXAMPLE 18

5.8 Parts of dichloro - (4 - hydroxynaphth - 1 _ yl)pyrimidine are dissolved in a solution of 2 parts of sodium hydroxide in 120 parts of water, the solution agitated vigorously and 30 parts of ice added followed by 3 parts of acetic anhydride. A further 1.4 parts of sodium hydroxide and 3 parts of acetic anhydride are added, agitation continued for 30 minutes and the product filtered off from the alkaline solution. It is purified by crystallisation from ethylene glycol monomethyl ether to give 3.9 parts of dichloro - (4 - acetoxynaphth - 1 - yl) pyrimidine melting between 185 and 187°C. Analysis gives C 57.8%, H 2.8%, N 8.2%, Cl 20.3%. C $_{16}H_{10}O_2Cl_2N_2$ requires C 57.7%, H 2.95%, N 8.4%, Cl 21.3%.

The product may be used to whiten cellulose acetate.

EXAMPLE 19

1 parts of 2:4 _ dichloro - 6 - (4 - methoxynaphthyl) - 1:3:5 - triazine is milled with 100 parts of water in presence of 0.2 parts of the sodium salt of an alkylated naphthalene sulphonic acid for 16 hours and then diluted with water to 500 parts. Polyester fabric is padded through this dispersion and is then dried at a temperature between 100 and 120°C. and heated at 180°C. for about 30 seconds. The fabric so obtained is whiter than untreated polyethylene terephthalate fabric.

EXAMPLE 20

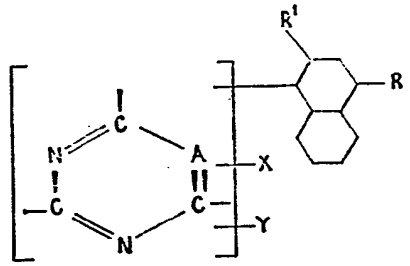
1 part of polyethyleneterephthalate fabric is suspended for 45 minutes in 30 parts of boiling water to which 1 part of the dispersion used in Example 19 has been added, and is then dried and heated at a temperature between 160°C. and 180°C. for 30 seconds. The fabric so obtained is whiter than untreated polyethyleneterephthalate fabric.

EXAMPLE 21

1 part of polyethylene terephthalate fabric is heated for 1 hour with 30 parts of water to which 1 part of the dispersion used in Example 19 has been added at a temperature between 120°C. and 140°C. under superatmospheric pressure. The fabric so obtained is whiter than untreated polyethylene terephthalate fabric.

WHAT WE CLAIM IS:—

1. New naphthalene compounds of the formula



wherein R and R^1 each stand for a hydrogen atom or an alkoxy, aralkoxy. aryloxy, or acyloxy group, not more than one of them standing for a hydrogen atom, A stands for a nitrogen atom or a group CB wherein B stands for a hydrogen atom or chlorine atom and X and Y stand for a halogen atom or an amino, substituted amino, alkoxy, substituted alkoxy, aryloxy, mercapto or substituted mercapto group.

2. New naphthalene compounds as claimed

in Claim 1 wherein one of R and R^1 stands for a hydrogen atom and the other for an alkoxy group.

3. New naphthalene compounds as claimed in Claim 2 wherein R stands for a methoxy group.

4. New naphthalene compounds as claimed in any of Claims 1 to 3 wherein X and Y each stand for a chlorine atom.

5. 2:4 - dichloro - 6 - (4 - methoxy-naphthyl) - 1:3:5 - triazine.

6. New naphthalene compounds substantially as hereinbefore described especially with reference to the foregoing Examples 1 to 18 or their obvious chemical equivalent.

7. A process for the manufacture of new naphthalene compounds as claimed in Claim 1 wherein X and Y stand for a halogen atom, wherein a cyanuric halide or 2:4:6 - trihalogenopyrimidine is interacted in approximately equimolecular proportions with a naphthalene carrying alkoxy, aralkoxy, or aryloxy, substituents in one or both of the 1 and 3 positions in presence of a Freidel-Crafts type catalyst.

8. A process for the manufacture of new naphthalene compounds as claimed in Claim 1 wherein X stands for a substituted amino, alkoxy, substituted alkoxy, aryloxy or substituted mercapto group and Y stands for the same group as X or for a halogen atom, wherein a cyanuric halide or 2:4:6 - trihalogenopyrimidine is interacted in approximately equimolecular proportions with a naphthalene carrying alkoxy, aralkoxy, or aryloxy, substituents in one or both of the 1 and 3 positions in presence of a Freidel-Crafts type catalyst, and the dihalogeno compound so obtained is interacted with an amine, alcohol, phenol, or mercaptan in presence of an acid binding agent.

9. A process for the manufacture of new naphthalene compounds as claimed in any of Claims 1 to 6 substantially as hereinbefore described especially with reference to the foregoing Examples 1 to 18 or their obvious chemical equivalent.

10. A process for the whitening of polymeric materials by the incorporation into the said polymeric material of a new naphthalene compound as claimed in any of the Claims 1 to 6.

11. A process as claimed in Claim 10 wherein the incorporation is carried out in the presence of other whitening agents.

12. A process as claimed in either of Claims 10 or 11 wherein the polymeric material is a synthetic polymer.

13. A process as claimed in either of Claims 10 or 11 wherein the polymeric material is an artificial polymer.

14. A process as claimed in any of the Claims 10 to 13 wherein the process is carried out from aqueous medium at a temperature of at least 40°C.

15. A process as claimed in claim 14 wherein the polymeric material is secondary cellulose acetate and the process is carried out at a temperature of about 85°C.

16. A process as claimed in Claim 14 wherein the polymeric material is a polyamide, cellulose triacetate, an acrylonitrile polymer or copolymer or a polyester and the process is carried out at a temperature between 95° and 100°C.

17. A process as claimed in Claim 14 wherein the polymeric material is stable at a temperature exceeding 100°C. and the process is carried out at a temperature between 100°C. and 140°C. provided that it is lower than the temperature at which the said polymeric material becomes unstable.

18. A process as claimed in Claims 10 to 12 wherein the polymeric material is impregnated with an aqueous suspension of the new naphthalene compound and then heated for a short time at a temperature between 150°C. and 200°C. and preferably at about 180°C.

19. A process as claimed in any of Claims 10 to 18 wherein the incorporation is carried out in presence of a surface active agent.

20. A process as claimed in Claim 19 wherein the surface active agent is soap.

21. A process as claimed in any of the Claims 10 to 20 wherein the incorporation is carried out in the presence of disperse dyestuffs.

22. A process as claimed in any of Claims 10 to 12 wherein the naphthalene compound is incorporated into the polymer when the latter is in molten or plasticised form.

23. A process for the whitening of polymeric materials substantially as hereinbefore described especially with reference to the foregoing Examples or their obvious chemical equivalent.

24. Polymeric materials which have been whitened by a process claimed in any of the Claims 10 to 23.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1956 Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.